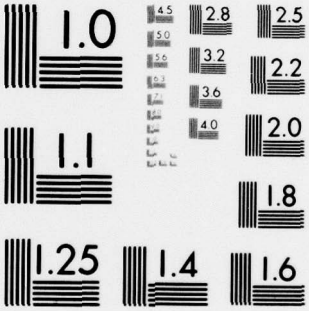
AD-A080 935 BROWN UNIV PROVIDENCE RI DEPT OF CHEMISTRY F/G 7/4
SPECTRAL STUDIES OF IONS IN PERFLUOROCARBONSULFONATE (NAFION) I--ETC(U)
DEC 79 S L PELUSO, A T TSATSAS, W M RISEN N00014-75-C-0883
UNCLASSIFIED TR-79-01 NL

| OF |

AD
A080935

END
DATE
FILMED
3 - 80
DDC



MICROCOPY RESOLUTION TEST CHART
NATIONAL BUREAU OF STANDARDS-1963-A

LEVEL II

(12)

OFFICE OF NAVAL RESEARCH

Contract ONR-N00014-75-C-0883 NR-051-539

TECHNICAL REPORT NO. TR-79-01

ADA080935

Spectral Studies of Ions in Perfluorocarbonsulfonate (Nafion) Ionomers

by

Susan L. Peluso, Andreas T. Tsatsas and William M. Risen, Jr.

Prepared for Publication

in the

Journal of Polymer Science (Polymer Physics)

December 10, 1979

Department of Chemistry
Brown University
Providence, RI 02912

DDC FILE COPY

December 10, 1979

DDC
RECEIVED
FEB 14 1980
D

Reproduction in whole or in part is permitted for
any purpose of the United States Government

Approved for Public Release; Distribution Unlimited.

80 2 14 009

UNCLASSIFIED

SECURITY CLASSIFICATION OF THIS PAGE (When Data Entered)

REPORT DOCUMENTATION PAGE

READ INSTRUCTIONS BEFORE COMPLETING FORM

1. REPORT NUMBER: TR-79-01 (14)

2. GOVT ACCESSION NO.

3. RECIPIENT'S CATALOG NUMBER: (9)

4. TITLE (and Subtitle): (6) Spectral Studies of Ions in Perfluorocarbon-sulfonate (Nafion) Ionomers •

5. TYPE OF REPORT & PERIOD COVERED: Technical rept.

6. PERFORMING ORG. REPORT NUMBER

7. AUTHOR(s): (10) Susan L. Peluso, Andreas T. Tsatsas and William M. Risen, Jr.

8. CONTRACT OR GRANT NUMBER(s): (15) N00014-75-C-0883, NR-051-539

9. PERFORMING ORGANIZATION NAME AND ADDRESS:
Department of Chemistry
Brown University
Providence, Rhode Island 02912

10. PROGRAM ELEMENT, PROJECT, TASK AREA & WORK UNIT NUMBERS

11. CONTROLLING OFFICE NAME AND ADDRESS:
Office of Naval Research
United States Navy
(11) 10

12. REPORT DATE: December 10, 1979

13. NUMBER OF PAGES: 29

14. MONITORING AGENCY NAME & ADDRESS (if different from Controlling Office): (12) 31

15. SECURITY CLASS. (of this report)

15a. DECLASSIFICATION/DOWNGRADING SCHEDULE

16. DISTRIBUTION STATEMENT (of this Report)

Distribution Unlimited; Approved for Public Release

17. DISTRIBUTION STATEMENT (of the abstract entered in Block 20, if different from Report)

18. SUPPLEMENTARY NOTES

19. KEY WORDS (Continue on reverse side if necessary and identify by block number)

ionomer, Nafion, Ion Motion, cations, infrared spectra

Accession For	
NTIS GRA&I	X
DDC TAB	
Unannounced	
Justification	
By	
Distribution/	
Availability Codes	
Dist.	Avail and/or special
A	

20. ABSTRACT (Continue on reverse side if necessary and identify by block number)

The infrared and far-infrared spectra of alkali, alkaline earth and transition metal ionomers of perfluorocarbonsulfonic acid (Nafion) polymers are reported. The cation motion features have been observed and the strength of the cation-site interactions determined. The effect of dehydration of the ionomers on cation-motion vibrations, cation-site bonding, and the nature of hydrogen bonding in the hydrated ionomers has been investigated.

DD FORM 1 JAN 73 1473 EDITION OF 1 NOV 65 IS OBSOLETE
S/N 0102-014-6601

UNCLASSIFIED

SECURITY CLASSIFICATION OF THIS PAGE (When Data Entered)

405436

Spectral Studies of Ions in Perfluorocarbonsulfonate (Nafion) Ionomers

Introduction

Ionic copolymers (ionomers) are versatile materials because the presence of ions in organic polymers influences their physical (1-3) and chemical (4) properties greatly. Of particular interest in their study is the nature of cation-polyanion interactions, how they are affected by hydration, degree of exchange, and ion clustering, and the effects that such interactions have on their viscoelastic, ion diffusion, catalytic, and related properties. Ionomers formed from hydrocarbon-based polymers have been investigated extensively. Their properties, which fall in rather narrow ranges, have been reviewed by Eisenberg (5) and others (6-8).

Recently ionomers based on a perfluorocarbon backbone with sidechains terminating in sulfonate groups have attracted considerable attention, which centers on the Nafion materials developed by the Du Pont Company for use as ion-exchangers and as separators in various electrochemical applications. Several of the important properties they have depend on the nature of the cation-site interactions.

We have reported studies of cation-site interactions in several ionomeric systems; polyethylene methacrylic acid (PEHA) and polystyrene methacrylic acid (PSMA) ionomers, and have shown how the strength of the interaction and other features measureable spectroscopically depend on the influence of hydration, clustering, and the nature of the cation and anionic polymer (9,10). The importance of the Nafion-type, or PFSA, ionomers demands that cation-motion, hydration, and similar effects in them be studied as well.

In addition to investigating the spectral behavior of PFSA ionomers for the reasons mentioned above, however, there is another reason of potential

significance. It derives from the fact that the perfluorinated chains impart an unusually high thermal and chemical stability to PFSA ionomers. If transition metal PFSA ionomers are prepared, and the transition metal sites rendered coordinatively unsaturated. The materials could then be reacted in the presence of either rather reactive molecules (taking advantage of the chemical stability) or weakly reactive molecules (taking advantage of the coordinative unsaturation attainable), and, in either event, new chemistry achieved. Clearly catalytic systems are achievable, in analogy to others known (11), and new synthetic, gas separation, and catalytic possibilities realized in these stable materials that are not realization in hydrocarbon-based ionomers.

To provide an understanding both of the ionic interactions important in present applications and of the role of certain transition metal species in PFSA ionomers, we have carried out an infrared study of Nafion ionomers with group Ia, IIa, and several transition metal cations.

In investigating ionic polymeric substrate-metal ion interactions we have chosen perfluorosulfonic acid copolymer, (PFSA) which may be represented as

$$-(CF_2CF_2)_n-(CF_2\underset{\displaystyle O-(CF_2\underset{\displaystyle CF_3}{\underset{|}{C}}F)_z-CF_2CF_2SO_3^-H^+}{\underset{|}{C}}F)-$$

where z is small (1-5) and n takes on values up to 13 for polymers with equivalent weights of 1100-1600. Summaries of some physical properties of this copolymer have been published (5).

Experimental

Perfluorosulfonic acid (PFSA) ionomers are of the form:

$$\left[-(CF_2CF_2)_n-(CF_2\underset{\displaystyle O-(CF_2-\underset{\displaystyle CF_3}{\underset{|}{C}}F-O)_z-CF_2CF_2SO_3^-}{\underset{|}{C}}F)-\right]_k M^{+k}$$

where M^{+k} is a group IA, group IIA or other cation, such as a transition metal ion. The samples were studied as films labelled by a symbol including the counterion followed, in parentheses, by a three digit number. The first two digits give the equivalent weight in hundreds and the last digit the nominal film thickness in thousandths of inches. For example, K(142) is a potassium ionomer film of 1400 equivalent weight and 2 mils thick.

The ionomers were prepared from the acid form of the polymer by ion exchange. Each film was emersed in an aqueous solution of the nitrate or chloride salt of group IA, IIA metals and transition metals for several hours. After removing the films from the solution they were rinsed well with distilled water. An alternate preparation involves using a solution of the appropriate base. The salt or base concentration is not very critical, but if nearly all acidic hydrogens are to be replaced are in excess of cations is required. The degree of replacement of sulfonic hydrogens by M^{+k} in the samples studied was ascertained by infrared spectroscopy to be 99-100%.

The infrared spectra in the 50-3800 cm^{-1} region were recorded with Digilab FTS-14 and FTS-15B Fourier transform infrared spectrometer at ambient temperatures. In the mid infrared region each trace represents the average of 64 scans. In the far-infrared each trace represents the average of 200-1000 scans. All spectra were obtained with ca. 2 cm^{-1} resolution and recorded several times with a reproducibility of better than 1% in absorbance.

Dehydration experiments were performed on wet films both in the mid and far infrared region. The films were mounted on a brass support inside a specially designed evacuable cell in which the temperature was variable from 20° to 240°C and measured and controlled to within 1°C. The cell was fitted with KBr or high density polyethylene windows. Spectra were taken at ambient temperatures before and after evacuating the cell and at various times during the dehydration process, during which the cell was pumped on continuously.

Spectral Results

Mid Infrared Spectra

Spectra of two partially hydrated and dehydrated acid form PFSA films are shown in Figure together with that of a completely exchanged and dry K (142) film. (Hydrated) Films 2 mils or greater in thickness appear almost totally opaque in the 3800-500 cm^{-1} region, but even th e l ml thick films have a broad ill defined band beginning in the OH stretching region and extending to ca. 1500 cm^{-1}. This band envelope is attributed to the extensive hydrogen bonding interactions involving the SO_3H groups[12] and H_2O and is more intense in wet films where the acidic protons can associate with water molecules to give $H_{2n+1}O_n^+$ moieties. Absent from the dried films are the bands in the 3500 cm^{-1} region due to symmetric and antisymmetric O-H vibrations of the water molecule and the band in the 1600-1700 cm^{-1} region due to the water bending vibration.

There are other subtle differences in the spectra of hydrated and dry films of the PFSA ionomers. A weak broad asymmetric band in the 1420 to 1450 cm^{-1} region for hydrated films becomes sharper, well defined and more intense in films that have been dried. This band is absent in films where H^+ has been totally exchanged for a metal ion and is thought to be either a stretching vibration of the SO bond with double bond character in the SO_3H group or a sulfonic O-H-O bending vibration between associated acid groups.

Another difference between the wet, dry and exchanged films is the shifting of the 870 cm^{-1} band to 920 cm^{-1} upon dehydrating as can be seen in Fig 21. This band is possibly a S-O stretch with single bond character and is absent in exchanged films which have only two bands at 980 cm^{-1} and at ca. 1060 cm^{-1} whose exact position depends on the cation. These bands are also observed in the acid form of the copolymer but the 980 band is clearly a doublet for the hydrated film. Fig. 2I.

Upon complete exchange of the acidic protons by a metal ion one observes that the infrared transmittance is greatly enhanced. The hydrated films have well defined bands in the OH stretching region and a band in the HOH bending region Fig. 3. These bands which can be completely eliminated by dehydrating the films Fig. 4 result from the water which hydrates the ions. Thus, a dehydrated (salt) exchanged film contains just one broad, asymmetric band at ca. 2360 cm^{-1} in the 1350 to 3800 cm^{-1} region. It is an overtone of the strong bands centered in the 1200 cm^{-1} region (12,13).

As evidenced by the intensity of the bands in the OH stretching region and the H-O-H bending band, water retention by the film depends on the size and charge of the cation as does the hydration of a cation. Hydration decreases as size increases and group IIa ion hydration is greater than that of group Ia and IIa exchanged films and only for Mg^{+2} films was removing the last traces of water difficult.

Far Infrared Spectra

The far infrared spectra of (50-300 cm^{-1}) of PFSA 115 ionomers of Na^+, K^+, Rb^+ and Cs^+ are shown in Figure 5 along with the spectrum the acid form of the copolymer. Each spectrum contains a broad, well defined band in the region below 300 cm^{-1} which is absent in the acid form. This band is somewhat masked in the case of the Na^+ ionomer by the 203 cm^{-1} internal mode of the PFSA copolymer backbone. The band shifts from 180±7cm^{-1} in the Na^+ ionomer to 150±5cm^{-1} for Cs^+. Similar shifts are observed with 125, 142 and 152 ionomer films. In Figure 6 are shown the spectra of the Mg^{+2}, Ca^{+2}, Sr^{+2} and Ba^{+2} ionomers. Again the well defined band observed at 125±5cm^{-1} for Ba (115) is shifted to 155±5cm^{-1} in Sr(115), 200±7cm^{-1} (with the common 203cm^{-1} band superimposed on it), in Ca(115) and ca. 240±7cm^{-1} in Mg^{+2}. The change in frequency of these bands can be accounted for largely by the change in mass, M, of the cation. The observed low frequency bands in the group Ia and group IIa PFSA ionomers is given in Figure 7, in which a correlation is shown between the frequencies of the cation-motion bands of

cations which have the approximately the same mass but differ in charge. Indeed, the frequency, ν, varies nearly linearly with $M^{-\frac{1}{2}}$ for PFSA ionomers as shown in Figure 8 for each group of ions. This linear dependence of ν on $M^{-\frac{1}{2}}$ indicates that the vibration is due to cation motion, and that the cation anionic site force constants are approximately the same for each ion in a given group but greater for group IIa cations than for group Ia cations. Furthermore, the correlation is quite consistent with the cation-site forces being essentially ionic in nature (9).

In Figure 9 are shown the far infrared spectra of K^+ ionomers of 152, 142, 125, 115 films. The spectra are normalized to constant absorbance of the 203cm^{-1} PFSA internal motion band (and offset for display). In the 152 and 142 PFSA films which have lower acid-group concentration, the cation motion bands, centered at 150±5cm^{-1}, exhibit considerable asymmetry to the low frequency side. As the acid group concentration increases, in going from an equivalent weight of 1500 to 1100, the cation motion band increases in intensity and the asymmetry on the low frequency side of the band disappears. The same asymmetry is clearly observed on the high side of the Rb(142) ionomer centered at ca 108±5cm^{-1}. One can, thus, conclude that the asymmetry is due to a low frequency polymer backbone vibration whose intensity does not increase as the ionic concentration increases and is observed only when the ion motion band is of low enough intensity. This is important to note in light of the cluster mode observed in the PSMA ionomers (14).

In order to determine whether the ion motion band was influenced by water within the film, dehydration studies of several types of K^+-PFSA films and Rb(125) film were undertaken. The results for a K(152) film are shown in Figure 10. No shift in the ion motion band or other internal motion bands occurs. Trace (c) represents the spectrum of a wet film from which the excess surface water was wiped off. Although it would seem that the ion motion band is more intense for

the wet film, its higher absorbance is due to water absorptions which are particularly strong in this spectral region. Trace (b) represents a partially dry film, which was produced by pumping on the cell for three hours at ambient temperature. The dry film (a), produced by heating to 150°C and pumping for 6 hours, gives a higher quality spectrum but no significant spectral changes are observed.

Transition Metal Ionomers

Since one future goal of studies of PFSA ionomers involves binding metal complexes in them and studying their structure, reactivity, and potential catalytic properties, it is important to know what the nature of the metal ion is in the PFSA film both before and after dehydration. Although detailed results for each ion studied will be discussed more appropriately in future papers, that deal with the chemistry at the metal sites, a few general results will be presented here.

Transition metal ionomers of Mn^{+2}, Fe^{+2}, Co^{+2}, Ni^{+2}, Cu^{+2} and Ag^{+} have been prepared by the same methods used to prepare the group Ia and IIa ionomers. For these and other transition metal ions one has to be concerned about the consequences of hydrolysis. Very concentrated metal salt solutions will have low pH and prevent complete exchange by suppressing the ionization of the sulfonic acid groups. Exchange of ions also causes a drop in pH so dilute solutions should be used and, if necessary the incompletely exchanged film should be recovered and placed in a fresh solution to complete the exchange.

As expected transition metal ionomer films containing the same concentration of SO_3^- groups as group Ia and IIa films retained more water and were harder to dehydrate. Indeed in some instances complete dehydration was not achieved even after heating the film at 240°C in an evacuated cell for several days. Figure 11 shows the spectrum of a Cu^{+2} ionomer as initially prepared from aqueous solution and at various stages of dehydration.

As is the case with the alkali and alkaline earth ionomers, the completely exchanged transition metal ionomers have only two bands in the region between 800 and 1100, whereas the acid form has three. This indicates the absence of S-O

bonds with single bond character. It is also of interest to know whether the $-SO_3^-$ groups are a part of the coordination sphere of the metal ion and, if so, where they mono or bidentate ligands.

For most group Ia and IIa ions the 980 cm^{-1} band is a sharp single peak indicating that the oxygen atoms of the SO_3^- group are equivalent and that, therefore, such ions lie at the midpoint between the three oxygen atoms. For polystyrene sulfonic acid salts Zundel (15) favors the attachment of a cation to a single oxygen atom only. Since this band is asymmetric for Cs^+ and Ba^{+2} ionomers (Figure 2) and clearly split for transition metal ionomers (Figure 2-III) one concludes that for steric reasons or because of possible covalent bonding of transition metals to the SO_3^- groups the local C_{3v} symmetry of the sulfonate group is reduced. This would indicate that SO_3^- ions are a part of the transition metal's coordination sphere and that bivalent cations provide crosslinks between polymeric chains. Water molecules are also a part of the coordination sphere since it is often difficult to completely dehydrate transition metal ionomers. However, contrary to our expectations the cobalt(II) hydrated ionomer had a visible spectrum identical to that of $[Co(H_2O)_6]^{+2}$ in aqueous solution as can be seen in Figure 12.

Conclusions

We have shown that the infrared spectrum a hydrated PFSA film shows some interesting changes upon dehydration. In the dry film the sulfonic proton is associated with one of the oxygen atoms and although clustering (5) of the acid group and hydrogen bonding among them is extensive there exist S-O bonds of single and double bond character as well as S-O bonds of intermediate bond order because of hydrogen exchange between oxygen atoms. In the wet film the sulfonic proton is to a large degree ionized, so that the sulfonic oxygens are essentially equivalent and $(H_{2n+1}O_n)^+$ moieties exist close to the anionic sites. This creates local C_{3v} symmetry for the SO_3^- group as is the case with the metal ion exchanged films except when steric effects or covalent bonding lower the symmetry. Thus, aside

from the enhanced transparency in the 3500-1300 cm^{-1} region arising from hydrogen bonding between sulfonic acid groups in the acid form, the hydrated PFSA films and their ionomers are structurally similar in that a hydrated proton or hydrated metal ion exists in the vicinity of the anion. Eisenberg and Yeo (1) have pointed out, however, that for these materials there is a dramatic decrease in density upon ionization accompanied by increase in the water diffusion coefficient in contrast to other ionomers. This indicates to us that the polymeric material swells to accommodate a hydrated or otherwise coordinated cation.

For the group Ia and IIa ionomers the interaction between the cation and the SO_3^- groups are essentially ionic in nature. The oxygen atoms of the sulfonate group are, in most cases, equivalent and the M^+ or M^{+2} ion is enclosed in a cage involving one or more SO_3^- groups, the polymeric backbone and ligand molecules, e.g. water, for hydrated films. The ion motion frequencies are significantly lower than for ethylene methacrylic acid copolymers (9,10) and for many ionic glasses (17,18) and do not change when the film is thoroughly dehydrated. This would indicate a weaker force field on the cation or a larger vibrating assembly and possible conformational changes of the polymeric backbone upon dehydration, to compensate for the loss of a neighbor such as a water molecule, so that the net force field remains the same in both a wet and dry film.

In the case of transition metal ionomers the SO_3^- group is almost certainly a part of the coordination sphere of the cation but whether it behaves as a monodentate, bidentate or even as a tridentate ligand has not yet been ascertained. The water in many hydrated ionomer films may be completely removed but the spectrum of the dehydrated material remains unchanged in the entire infrared region except for the obvious suppression of water bands. Whether the polymeric backbone will undergo conformational changes, such as bi or tridentate binding of the anion to the cation, to compensate for loss of a ligand is still a question to be answered. However, experiments performed to date indicate that a procedure such as dehydrating a transition metal ionomer will leave the ion in a coordinatively

unsaturated state, a state of enhanced ability to bind and react with other species. Cu^{+2} ionomer films not only react with NH_3 which is a strong ligand but also with gaseous CO and NO to form novel compounds.

Acknowledgment

This work was supported in part by the Office of Naval Research. The partial support of the Materials Research Laboratory, sponsored by the National Science Foundation, is also gratefully acknowledged. The authors are grateful to Mr. George Rouse and Ms. Jane Lillienthal for helpful discussions and experimental assistance.

References

1. S. C. Yeo and A. Eisenberg, J. Appl. Polym. Sci., 21, 875 (1977).
2. W. Grot, Chem. Ing. Tech., 44, 167 (1972), ibid., 47, 617 (1975).
3. M. Lopez, B. Kipling and H. L. Yeager, Anal. Chem., 48, 1120 (1976).
4. D. J. Vaughn, duPont Innovation 4(3), 10 (1973).
5. Ion-Containing Polymers, Vol 2 of Polymer Physics, A. Eisenberg and M. King, Academic Press, New York 1977.
6. A. Eisenberg, Advan. Polym. Sci., 5, 59 (1967).
7. E. P. Otocka, J. Macromol. Sci. Rev., C5, 275 (1971).
8. L. Holliday, Ed., Ionic Polymers, Applied Science Publishers, London 1975.
9. A. Tsatsas, J. Reed and W. M. Risen, Jr., J. Chem. Phys., 55, 3260 (1971).
10. A. Tsatsas and W. M. Risen, Jr., Chem. Phys. Letters 7, 354 (1970).
11. E. Tsuchida and H. Nishide in "Advances in Polymer Science" Volume 24, pp 1-87, Springer Verlag, Berlin-Heidelberg, 1977.
12. S. Krimm and C. Y. Liang, J. Chem. Phys. 25, 563 (1956).
13. R. E. Moynihan, J. Am. Chem. Soc., 81, 1045 (1959).
14. G. B. Rouse, A. T. Tsatsas, A. Eisenberg and W. M. Risen, Jr., J. Polym. Sci., 17, 81 (1979).

15. G. Zundel, Hydration and Intermolecular Interaction, Chap V.11 Academic Press, New York, 1969.

16. G. J. Exarhos and W. M. Risen, Jr., Chem. Phys. Letters, 10, 484 (1971).

17. G. J. Exarhos and W. M. Risen, Jr., Solid State Commun., 11, 755 (1972).

Figure Captions

Figure 1. Mid infrared (3800-400 cm^{-1}) spectra of two hydrated and dehydrated H^+-PFSA films together with the spectrum of a dehydrated K^+-PFSA film in the 3800-1400 cm^{-1} region.

Figure 2. I. Spectra of an H(151) film: —— hydrated film, ... partially dehydrated film, —·— dehydrated film.

II. Spectra of Na^+ and Ba^{+2} ionomers in the 1100-800 cm^{-1} region: —— Na(151), ····· Ba(151). Spectra of hydrated and dry ionomer films are virtually identical in this region.

III. Spectra of some PFSA-142 ionomers in the 1100-800 cm^{-1} region: Li(142), Ba(142), Cu(142).

Figure 3. Spectra of PFSA-161 group Ia and IIa hydrated ionomers showing relative intensities of water stretching and bending bands.

Figure 4. Spectra of a K^+(142) ionomer film showing decrease in water band intensities upon dehydration: a. hydrated film, b. partially dried film, c. dry film.

Figure 5. Far infrared (50-300 cm^{-1}) spectra of PFSA-115 acid form copolymer and group Ia ionomers.

Figure 6. Far infrared (50-300 cm^{-1}) spectra of PFSA-151 group IIa ionomers.

Figure 7. Correlation of low frequency ion motion bands between group Ia and IIa ionomers having approximately equal mass.

Figure 8. Variation of ion motion frequency as a function of $M^{-1/2}$ for group Ia and IIa ionomers.

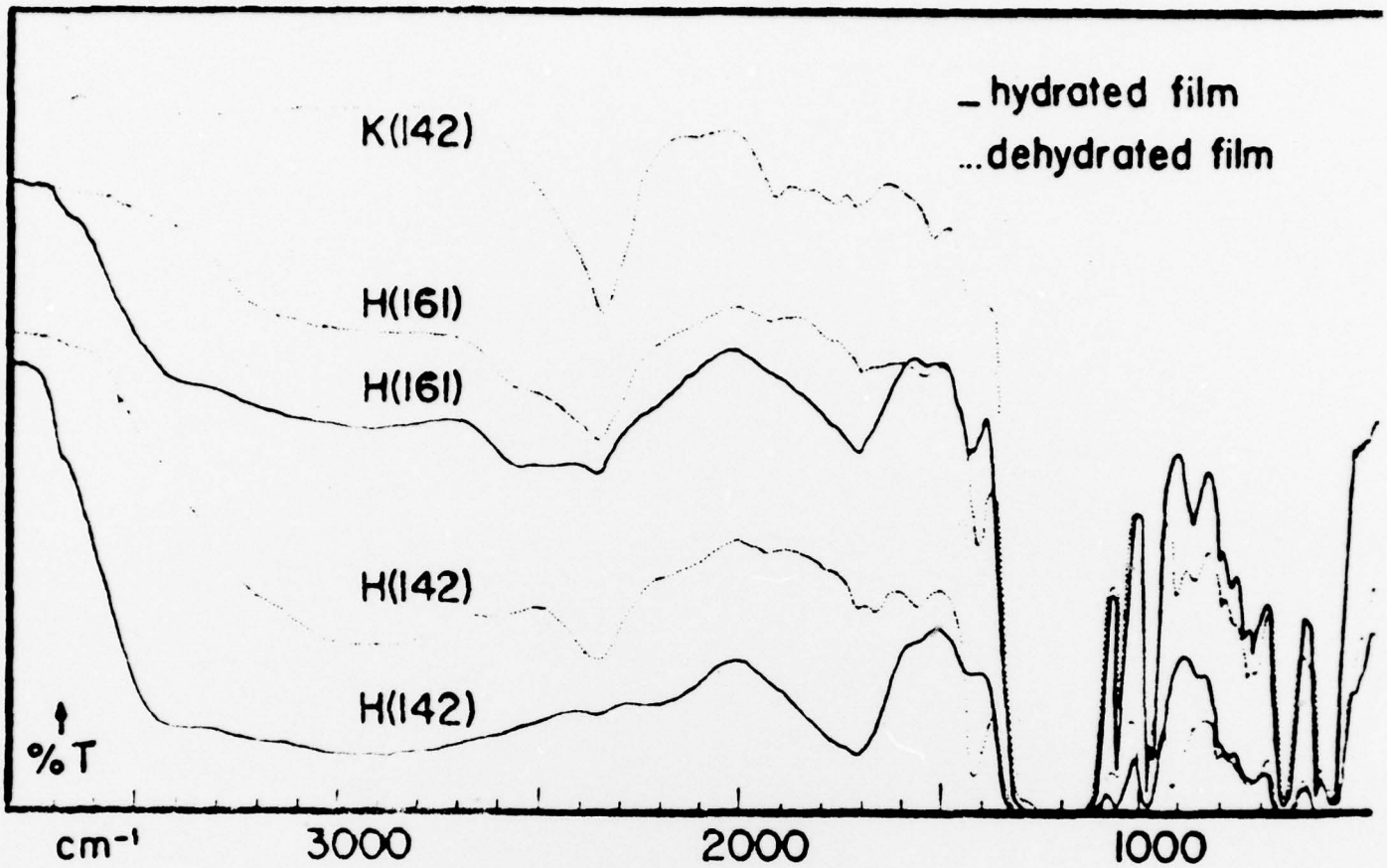
Figure 9. Far infrared (50-300 cm^{-1}) spectra of PFSA-K^+ ionomers.

Figure 10. Far infrared (50-300 cm^{-1}) spectra of a PFSA-K(152) ionomer: a. dry film, b. partially dried film, c. hydrated film.

Figure 11. Mid infrared (3800-400 cm^{-1}) spectra of a PFSA-Cu(142) ionomer at various stages of dehydration. a. fully hydrated film, b. partially dehydrated film after heating at ca. 140°C for three hours and continuous pumping, c. further dehydrated film after heating at 175° for three more hours, d. film after heating at 240°C for four more hours.

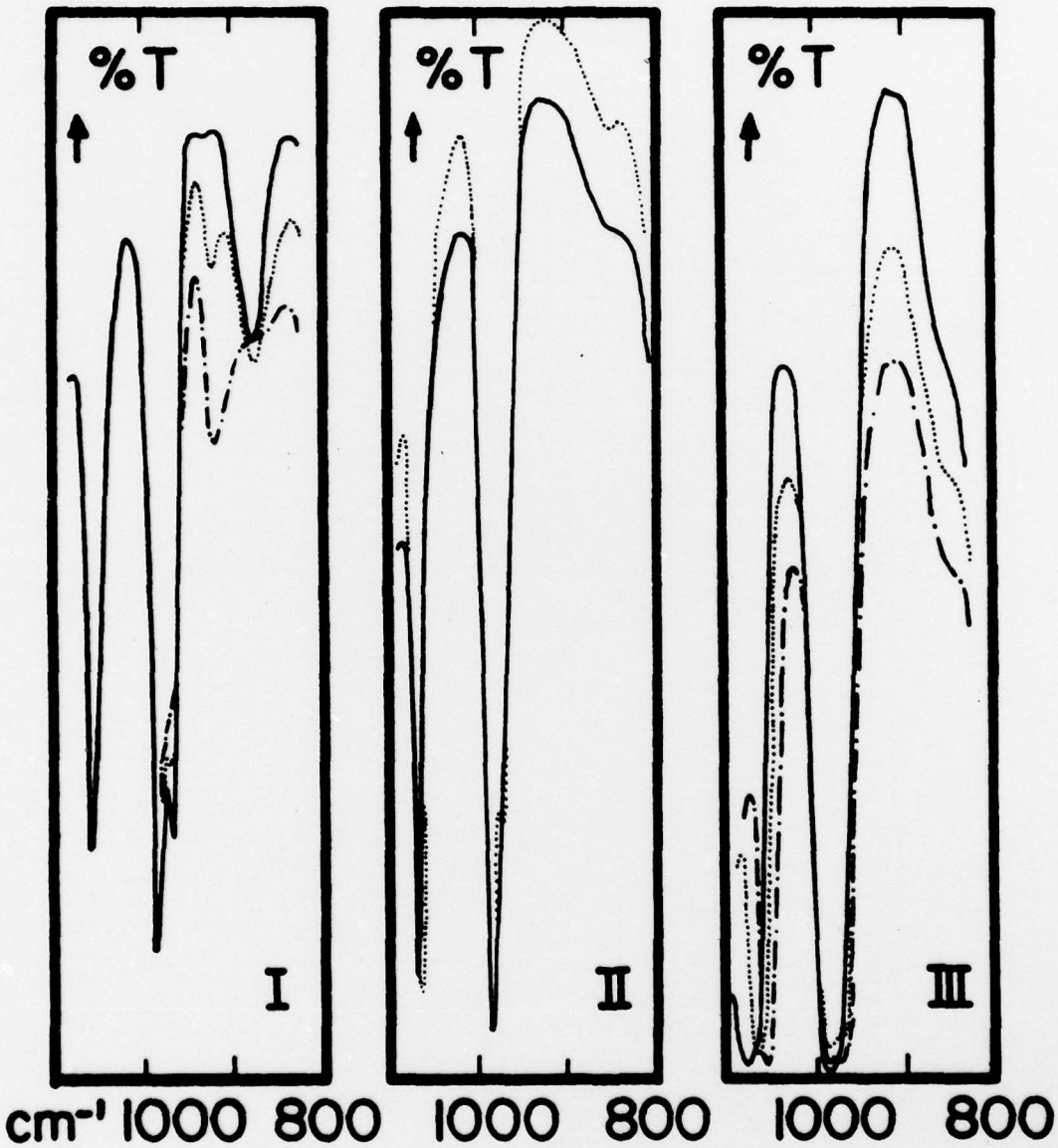
Figure 12. Visible spectra 600-400 nm. a. PFSA-H(125) film, b. fully exchanged PFSA-Co(125) ionomer film, c. resultant curve after subtracting absorbances of curve a from curve b, d. 0.01M $Co(NO_3)_2$ aqueous solution $[Co(H_2O)_o]^{+2}$.

FIGURE 1



Mid infrared (3800-400 cm^{-1}) spectra of two hydrated and dehydrated H^+-PFSA films together with the spectrum of a dehydrated K^+-PFSA film in the 3800-1400 cm^{-1} region.

FIGURE 2



I. Spectra of an H(151) film: —— hydrated film, ...partially dehydrated film,——·—— dehydrated film.

II. Spectra of Na^{+} and Ba^{+2} ionomers in the 1100-800 cm^{-1} region: —— Na(151), ...Ba(151). Spectra of hydrated and dry ionomer films are virtually identical in this region.

III. Spectra of some PFSA-142 ionomers in the 1100-800 cm^{-1} region: Li(142), Ba(142), Cu(142).

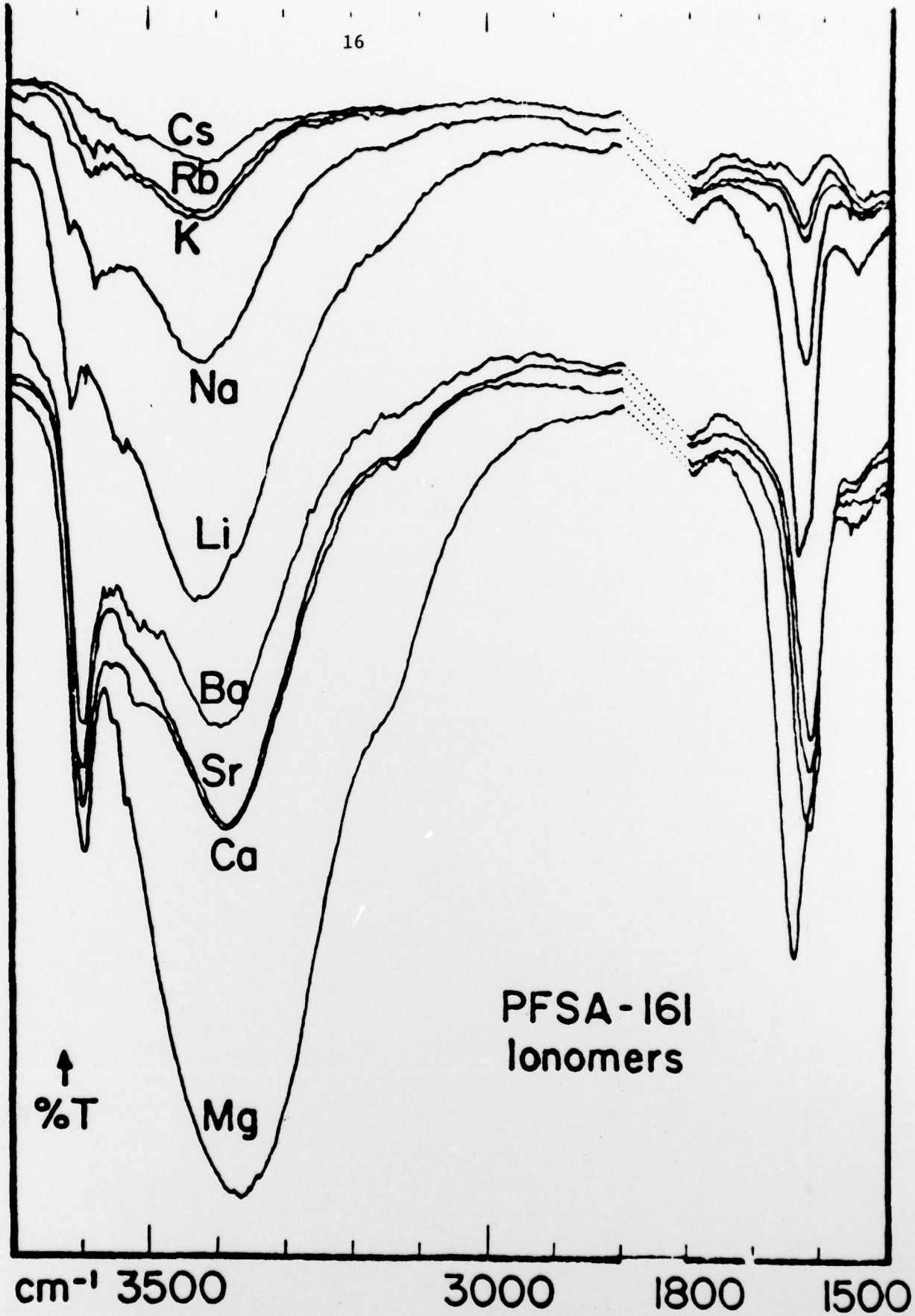


FIGURE 3

Spectra of PFSA-161 group Ia and IIa hydrated ionomers showing relative intensities of water stretching and bending bands.

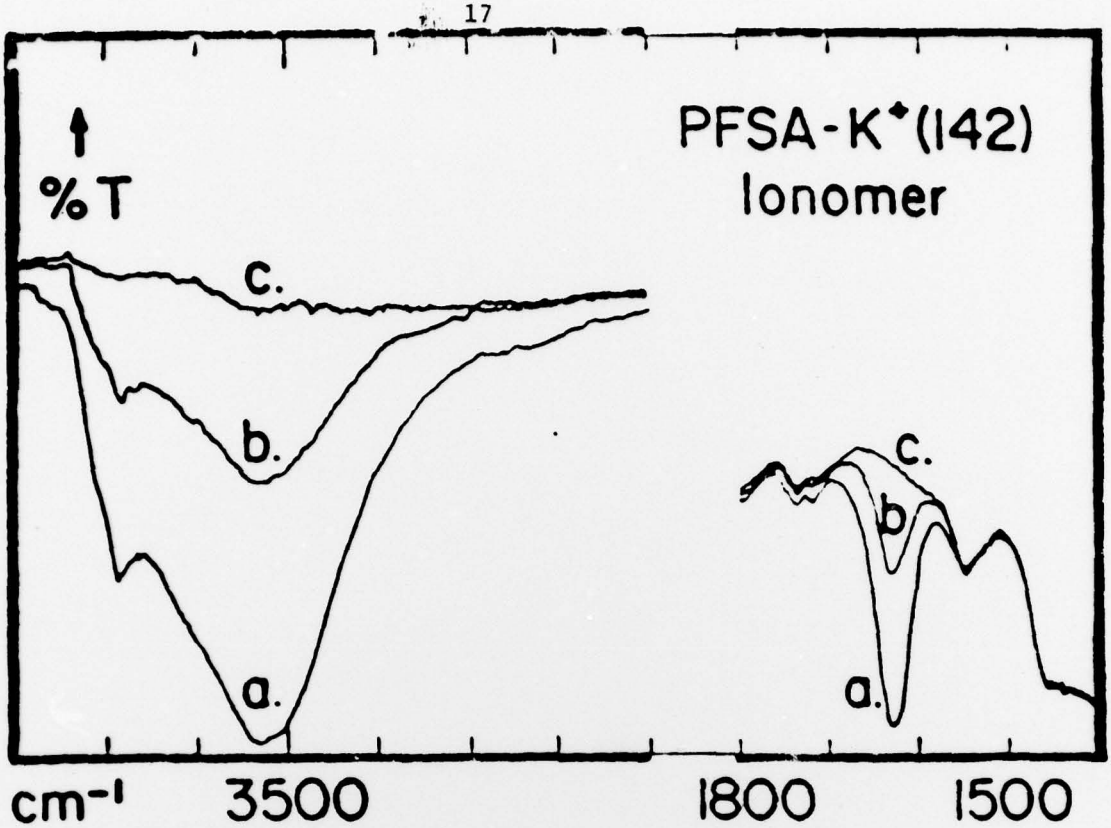


FIGURE 4

Spectra of a K^+(142) ionomer film showing decrease in water band intensities upon dehydration: a. hydrated film, b. partially dried film, c. dry film.

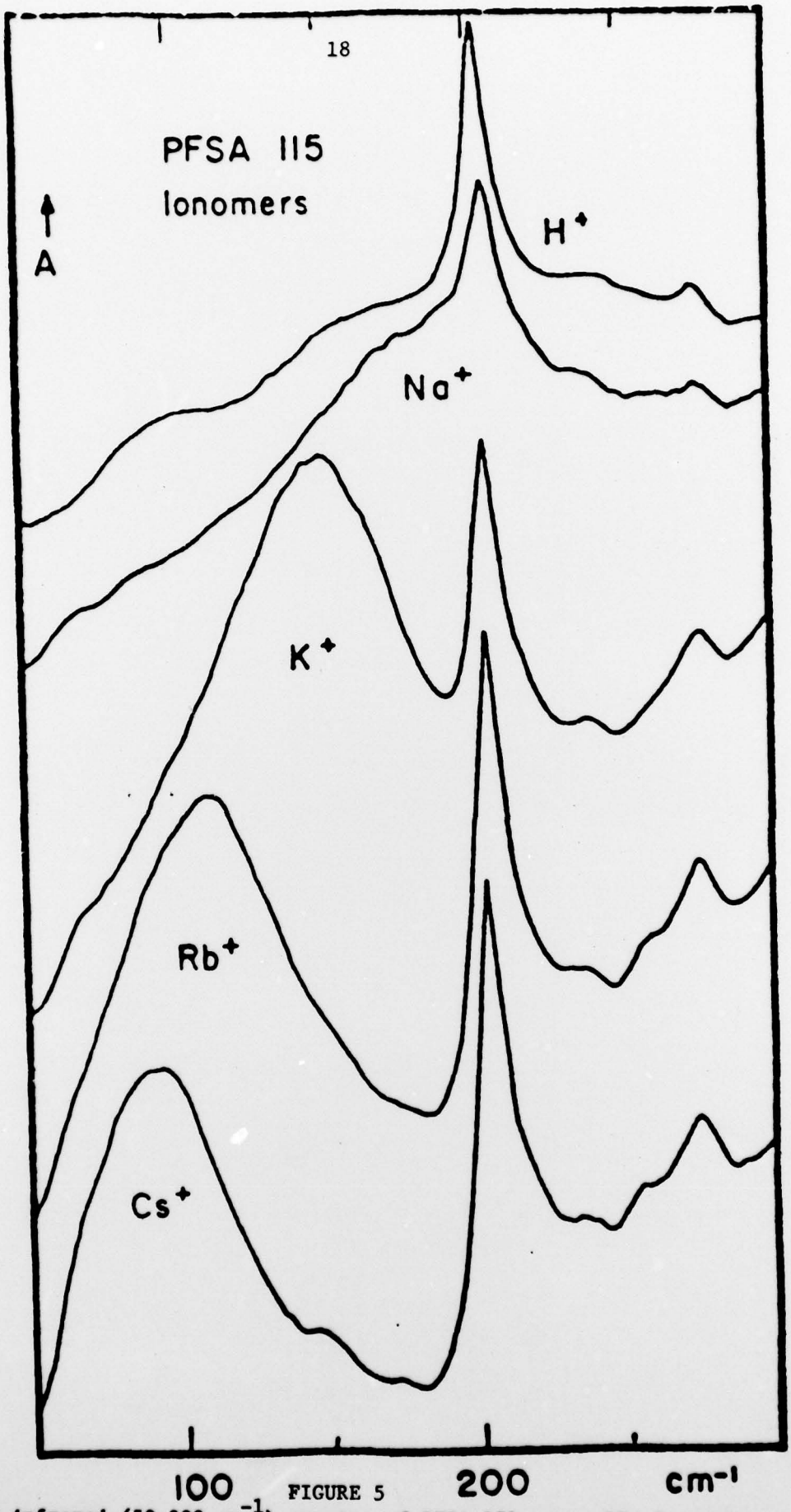


FIGURE 5

Far infrared (50-300 cm^{-1}) spectra of PFSA-151 group IIa ionomers.

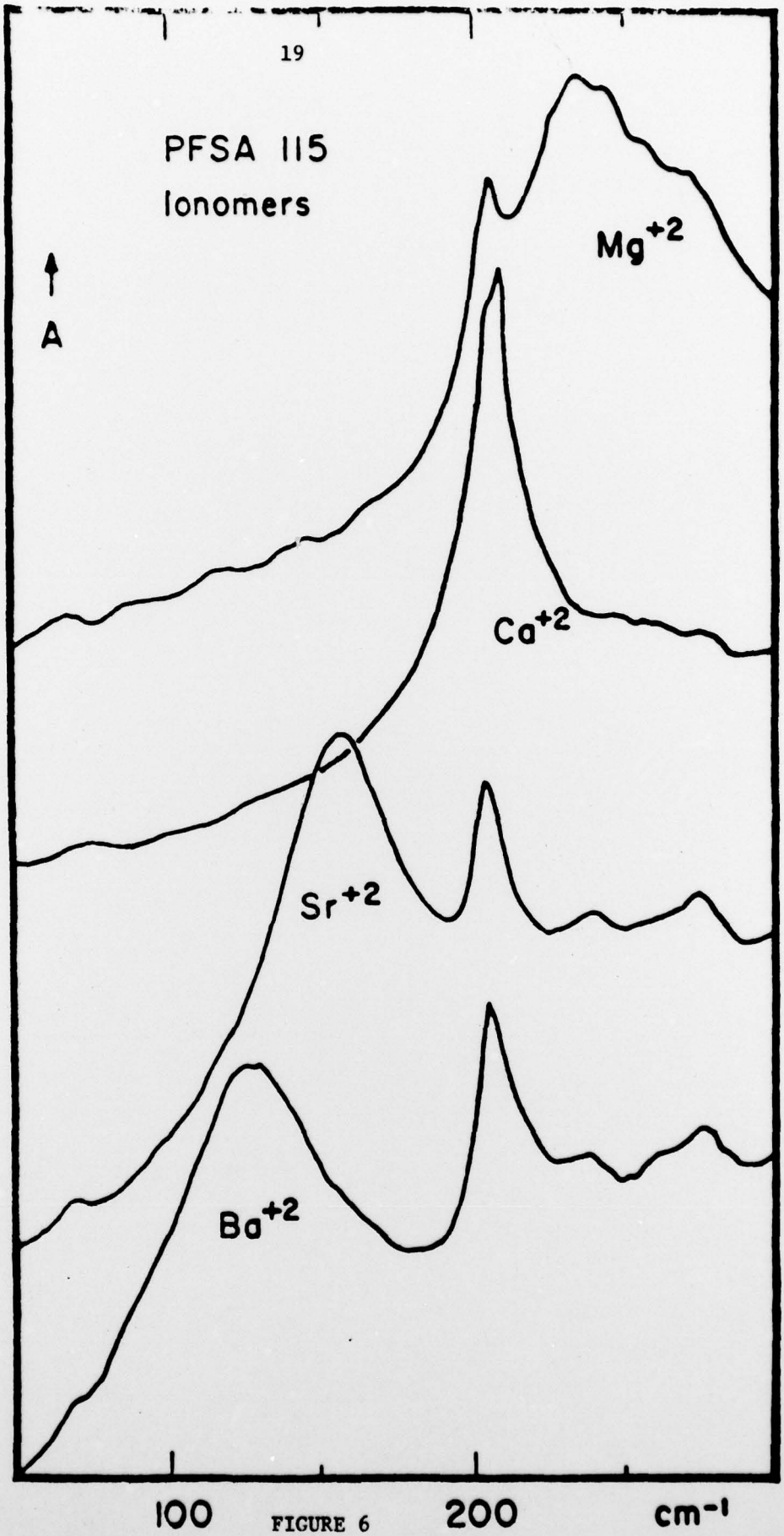
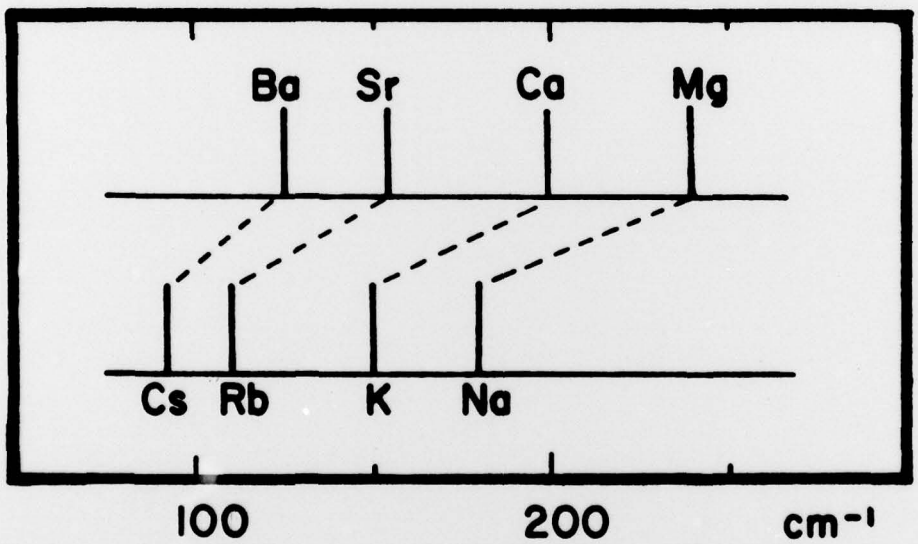


FIGURE 6

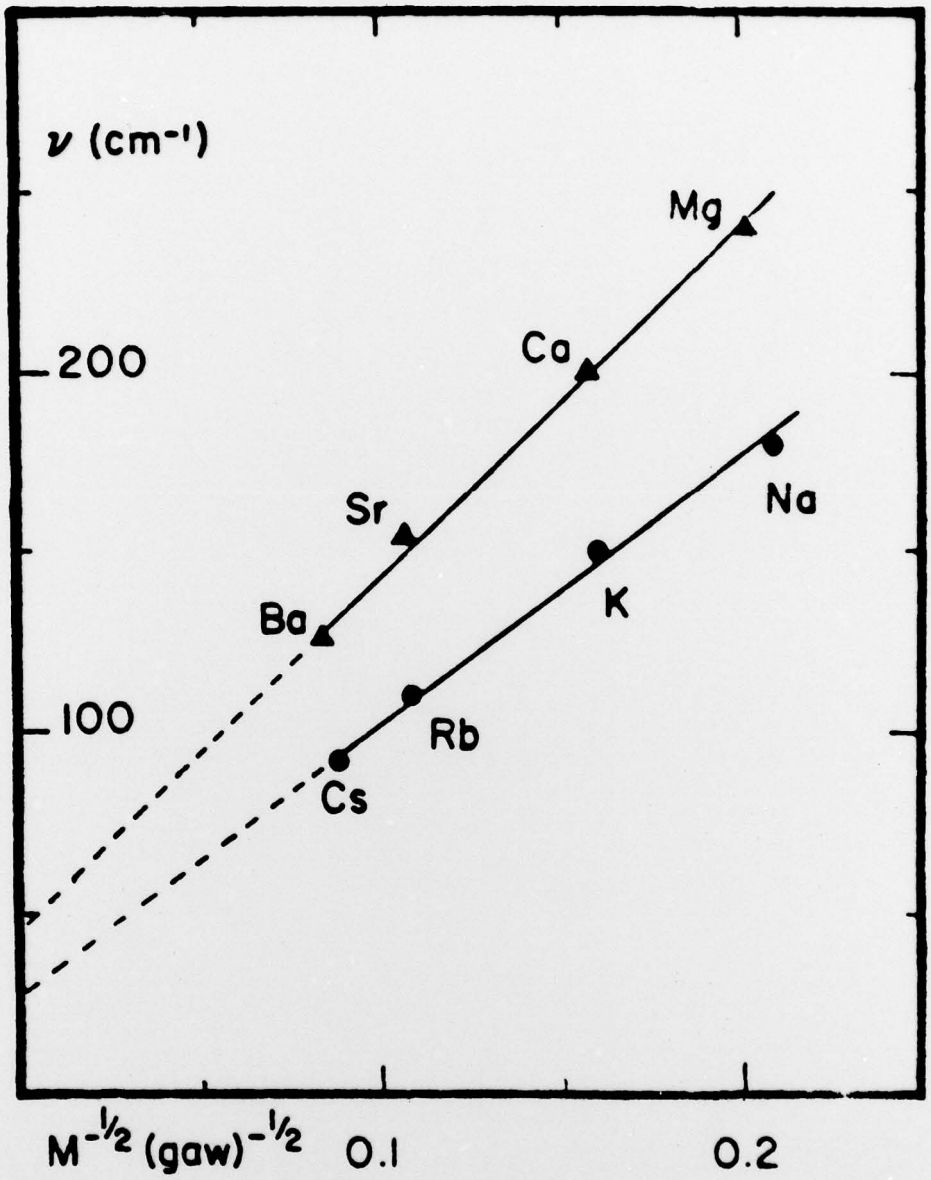
Far infrared (50-300 cm^{-1}) spectra of PFSA-151 group IIa ionomers.

FIGURE 7



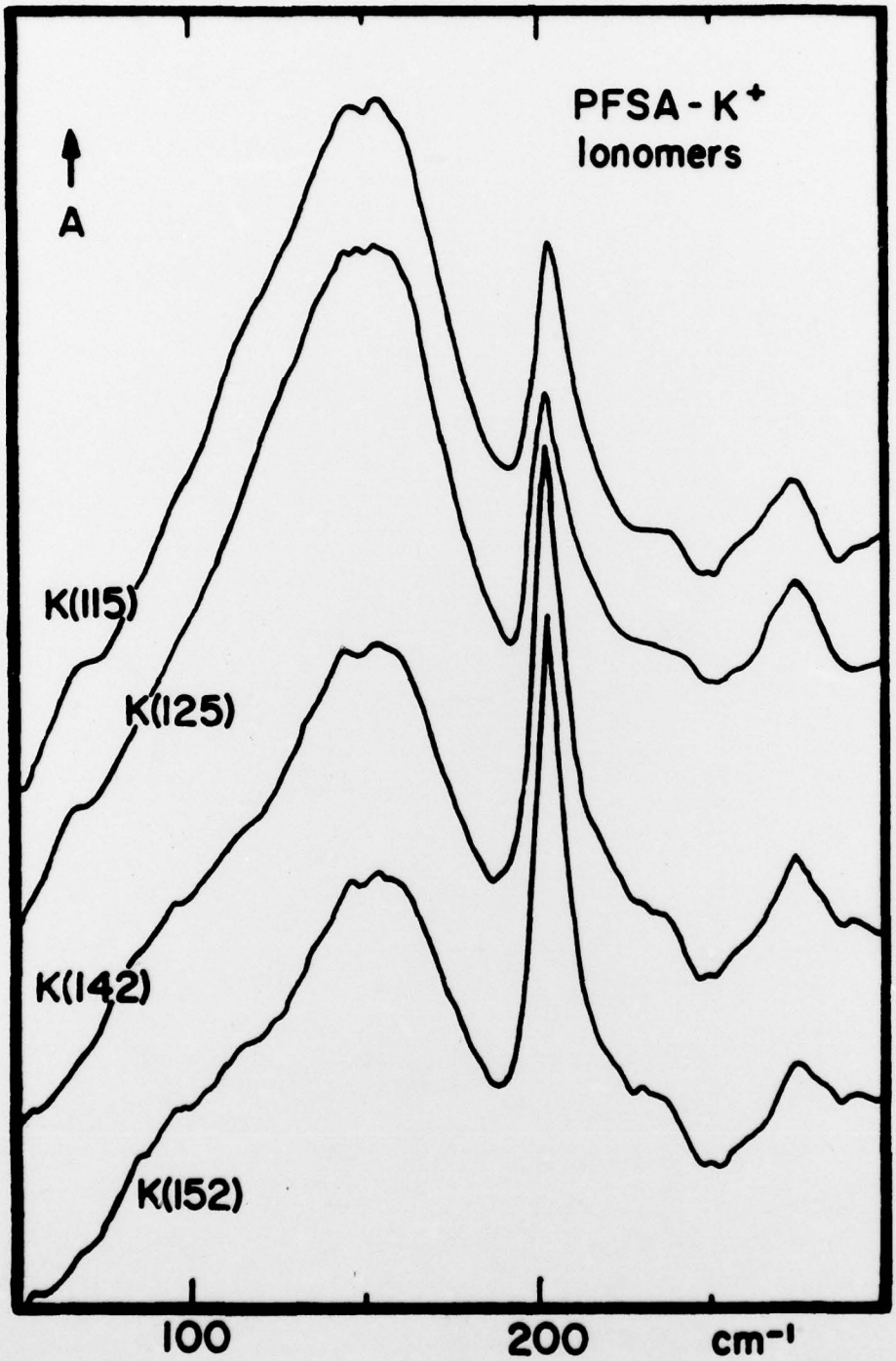
Correlation of low frequency ion motion bands between group Ia and IIa ionomers having approximately equal mass.

FIGURE 8



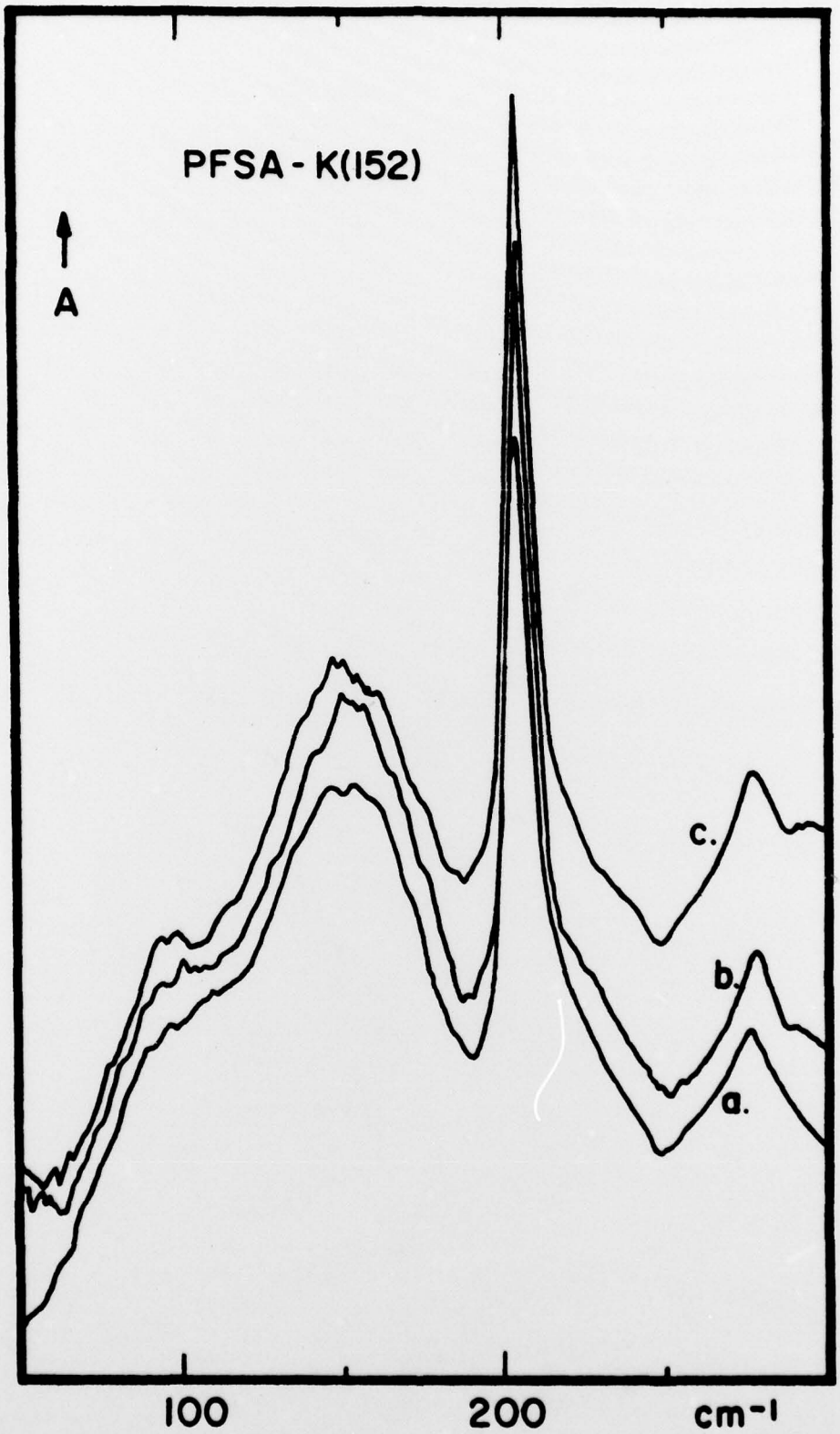
Variation of ion motion frequency as a function of $M^{-\frac{1}{2}}$ for group Ia and IIa ionomers.

FIGURE 9



Far infrared (50-300 cm^{-1}) spectra of PFSA-K^+ ionomers.

FIGURE 10



Far infrared (50-300 cm^{-1}) spectra of a PFSA-K(152) ionomer: a. dry film, b. partially dried film, c. hydrated film.

FIGURE 11

Mid infrared (3800-400 cm^{-1}) spectra of a PFSA-Cu(142) ionomer at various stages of dehydration. a. fully hydrated film, b. partially dehydrated film after heating at ca. 140°C for three hours and continuous pumping, c. further dehydrated film after heating at 175° for three more hours, d. film after heating at 240°C for four more hours.

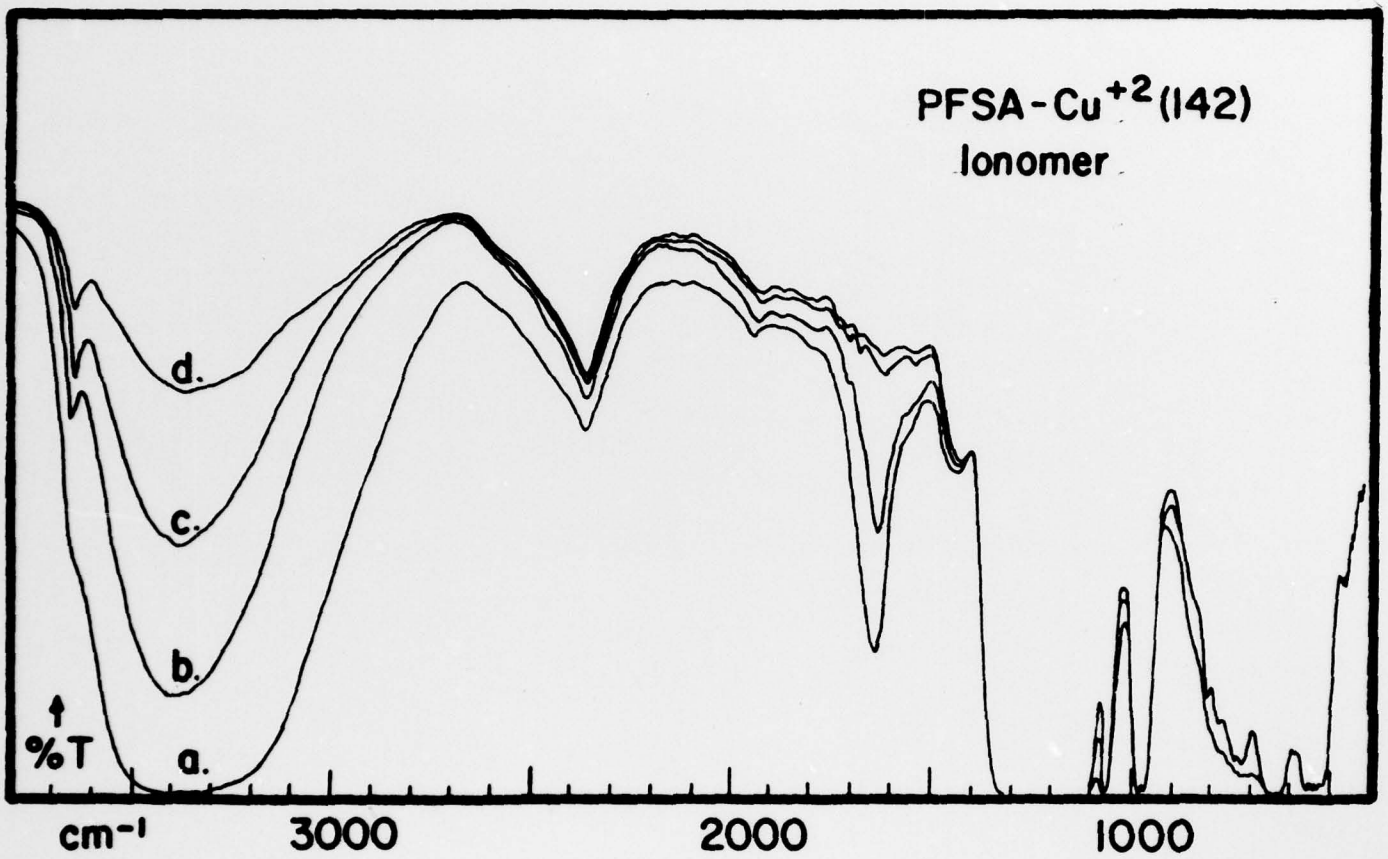
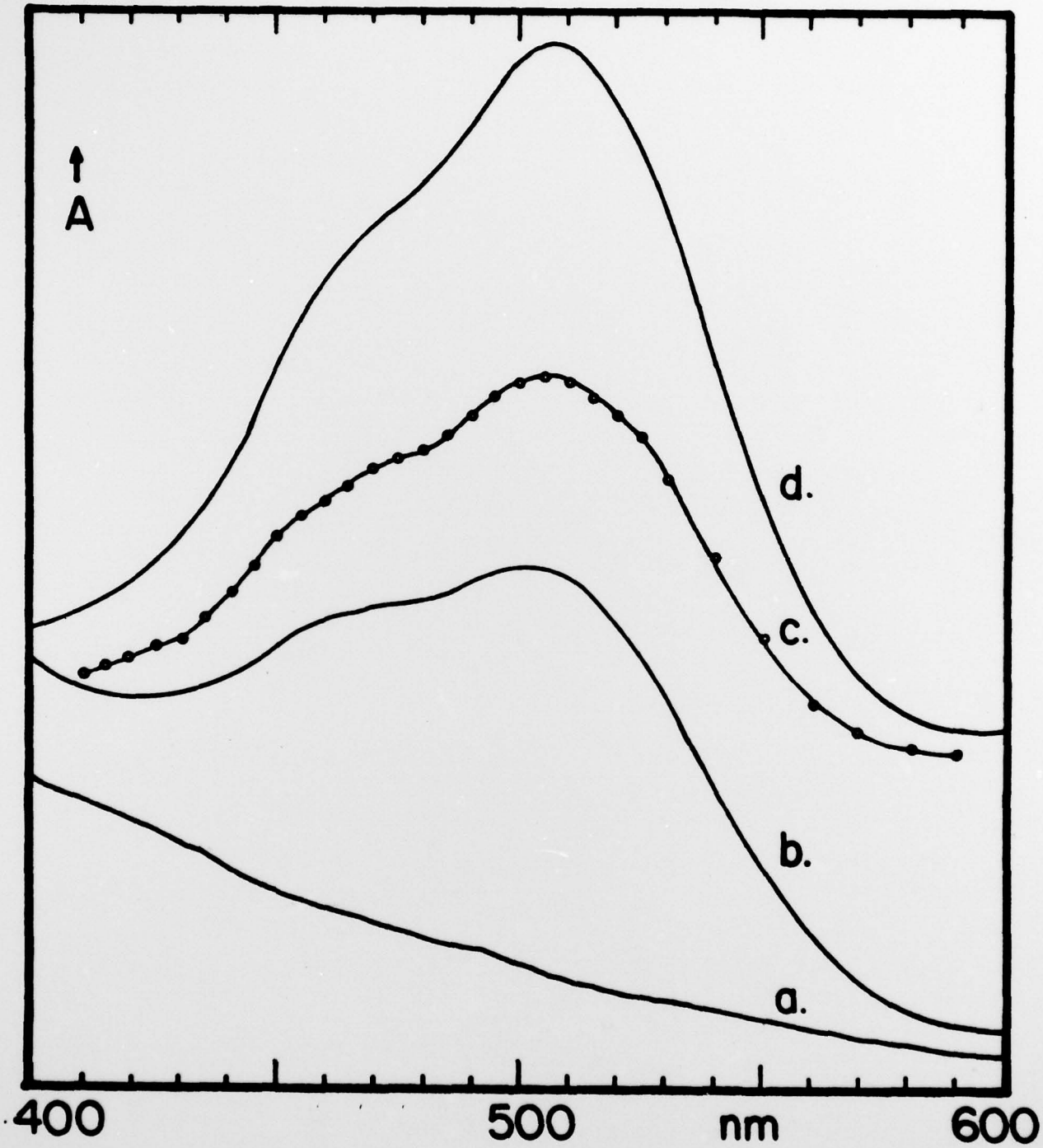


FIGURE 12



Visible spectra 600-400 nm. a. PFSA-H(125) film, b. fully exchanged PFSA-Co(125) ionomer film, c. resultant curve after subtracting absorbances of curve a from curve b, d. 0.01M $Co(NO_3)_2$ aqueous solution $[Co(H_2O)_6]^{+2}$.

TECHNICAL REPORT DISTRIBUTION LIST, GEN

	No. Copies
Office of Naval Research Attn: Code 472 800 North Quincy Street Arlington, Virginia 22217	2
ONR Branch Office Attn: Dr. George Sandoz 536 S. Clark Street Chicago, Illinois 60605	1
ONR Branch Office Attn: Scientific Dept. 715 Broadway New York, New York 10003	1
ONR Branch Office 1030 East Green Street Pasadena, California 91106	1
ONR Branch Office Attn: Dr. L. H. Peebles Building 114, Section D 666 Summer Street Boston, Massachusetts 02210	1
Director, Naval Research Laboratory Attn: Code 6100 Washington, D.C. 20390	1
The Assistant Secretary of the Navy (R,E&S) Department of the Navy Room 4E736, Pentagon Washington, D.C. 20350	1
Commander, Naval Air Systems Command Attn: Code 310C (H. Rosenwasser) Department of the Navy Washington, D.C. 20360	1
Defense Documentation Center Building 5, Cameron Station Alexandria, Virginia 22314	12
Dr. Fred Saalfeld Chemistry Division Naval Research Laboratory Washington, D.C. 20375	1
U.S. Army Research Office Attn: CRD-AA-IP P.O. Box 1211 Research Triangle Park, N.C. 27709	
Naval Ocean Systems Center Attn: Mr. Joe McCartney San Diego, California 92152	
Naval Weapons Center Attn: Dr. A. B. Amster, Chemistry Division China Lake, California 93555	
Naval Civil Engineering Laboratory Attn: Dr. R. W. Drisko Port Hueneme, California 93401	
Department of Physics & Chemistry Naval Postgraduate School Monterey, California 93940	
Dr. A. L. Slafkosky Scientific Advisor Commandant of the Marine Corps (Code RD-1) Washington, D.C. 20380	
Office of Naval Research Attn: Dr. Richard S. Miller 800 N. Quincy Street Arlington, Virginia 22217	
Naval Ship Research and Development Center Attn: Dr. G. Bosmajian, Applied Chemistry Division Annapolis, Maryland 21401	
Naval Ocean Systems Center Attn: Dr. S. Yamamoto, Marine Sciences Division San Diego, California 91232	
Mr. John Boyle Materials Branch Naval Ship Engineering Center Philadelphia, Pennsylvania 19112	

TECHNICAL REPORT DISTRIBUTION LIST, GEN

	No. Copies
Dr. Rudolph J. Marcus Office of Naval Research Scientific Liaison Group American Embassy APO San Francisco 96503	1
Mr. James Kelley DTNSRDC Code 2803 Annapolis, Maryland 21402	1

472:GAN:716:abc
78u472-608

TECHNICAL REPORT DISTRIBUTION LIST, 356A

	No. Copies
Dr. Stephen H. Carr Department of Materials Science Northwestern University Evanston, Illinois 60201	1
Dr. M. Broadhurst Bulk Properties Section National Bureau of Standards U.S. Department of Commerce Washington, D.C. 20234	2
Dr. T. A. Litovitz Department of Physics Catholic University of America Washington, D.C. 20017	1
Professor G. Whitesides Department of Chemistry Massachusetts Institute of Technology Cambridge, Massachusetts 02139	1
Professor J. Wang Department of Chemistry University of Utah Salt Lake City, Utah 84112	1
Dr. V. Stannett Department of Chemical Engineering North Carolina State University Raleigh, North Carolina 27607	1
Dr. D. R. Uhlmann Department of Metallurgy and Material Science Massachusetts Institute of Technology Cambridge, Massachusetts 02139	1
Naval Surface Weapons Center White Oak Silver Spring, Maryland 20910 Attn: Dr. J. M. Augl Dr. B. Hartman	1
Dr. G. Goodman Globe Union Incorporated 5757 North Green Bay Avenue Milwaukee, Wisconsin 53201	1
Picatinny Arsenal SMUPA-FR-M-D Dover, New Jersey 07801 Attn: A. M. Anzalone Building 3401	1
Dr. J. K. Gillham Princeton University Department of Chemistry Princeton, New Jersey 08540	1
Douglas Aircraft Co. 3855 Lakewood Boulevard Long Beach, California 90846 Attn: Technical Library Cl 290/36-84 AUTO-Sutton	1
Dr. E. Baer Department of Macromolecular Science Case Western Reserve University Cleveland, Ohio 44106	1
Dr. K. D. Pae Department of Mechanics and Materials Science Rutgers University New Brunswick, New Jersey 08903	1
NASA-Lewis Research Center 21000 Brookpark Road Cleveland, Ohio 44135 Attn: Dr. T. T. Serofini, MS-49-1	1
Dr. Charles H. Sherman, Code TD 121 Naval Underwater Systems Center New London, Connecticut	1
Dr. William Risen Department of Chemistry Brown University Providence, Rhode Island 02192	1
Dr. Alan Gent Department of Physics University of Akron Akron, Ohio 44304	1

472:GAN:716
78u472-608

TECHNICAL REPORT DISTRIBUTION LIST, 356A

	No. Copies
Mr. Robert W. Jones Advanced Projects Manager Hughes Aircraft Company Mail Station D 132 Culver City, California 90230	1
Dr. C. Giori IIT Research Institute 10 West 35 Street Chicago, Illinois 60616	1
Dr. M. Litt Department of Macromolecular Science Case Western Reserve University Cleveland, Ohio 44106	1
Dr. R. S. Roe Department of of Materials Science and Metallurgical Engineering University of Cincinnati Cincinnati, Ohio 45221	1
Dr. Robert E. Cohen Chemical Engineering Department Massachusetts Institute of Technology Cambridge, Massachusetts 02139	1
Dr. David Roylance Department of Materials Science and Engineering Massachusetts Institute of Technology Cambridge, Massachusetts 02039	1
Dr. T. P. Conlon, Jr., Code 3622 Sandia Laboratories Sandia Corporation Albuquerque, New Mexico	1
Dr. Martin Kaufmann, Head Materials Research Branch, Code 4542 Naval Weapons Center China Lake, California 93555	1
Professor S. Senturia Department of Electrical Engineering Massachusetts Institute of Technology Cambridge, Massachusetts 02139	1

	N Cop
Dr. T. J. Reinhart, Jr., Chief Composite and Fibrous Materials Branch Nonmetallic Materials Division Department of the Air Force Air Force Materials Laboratory (AFSC) Wright-Patterson Air Force Base, Ohio	4
Dr. J. Lando Department of Macromolecular Science Case Western Reserve University Cleveland, Ohio 44106	
Dr. J. White Chemical and Metallurgical Engineering University of Tennessee Knoxville, Tennessee 37916	
Dr. J. A. Manson Materials Research Center Lehigh University Bethlehem, Pennsylvania 18015	
Dr. R. F. Helmreich Contract RD&E Dow Chemical Co. Midland, Michigan 48640	
Dr. R. S. Porter University of Massachusetts Department of Polymer Science and Engineering Amherst, Massachusetts 01002	
Professor Garth Wilkes Department of Chemical Engineering Virginia Polytechnic Institute and State University Blacksburg, Virginia 24061	
Dr. Kurt Baum Fluorochem Inc. 6233 North Irwindale Avenue Azuza, California 91702	
Professor C. S. Paik Sung Department of Materials Sciences and Engineering Room 8-109 Massachusetts Institute of Technology Cambridge, Massachusetts 02139	